



# Spatial and temporal trends in the ecological risk posed by polycyclic aromatic hydrocarbons in Mediterranean Sea sediments using large-scale monitoring data

C. Rizzi<sup>a</sup>, S. Villa<sup>a,\*</sup>, C. Chimera<sup>a</sup>, A. Finizio<sup>a</sup>, G.S. Monti<sup>b</sup>

<sup>a</sup> Department of Earth and Environmental Sciences DISAT, University of Milano-Bicocca, Piazza della Scienza 1, 20126 Milano, Italy

<sup>b</sup> Department of Economics, Management and Statistics, University of Milano – Bicocca, Via Bicocca degli Arcimboldi 8, 20126 Milano, Italy

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## ABSTRACT

Benthic organisms play an important role in aquatic ecosystems and are often used as indicators of toxic environments. In this study, we reconstructed the spatial and temporal trend of risk to benthic communities living in sediments of the Mediterranean Sea posed by the presence of 16 polycyclic aromatic hydrocarbons (PAHs). Moreover, the origins of PAH contamination in the sea were also investigated. The analysis included multiple steps, starting with an in-depth review of available studies (from the early 1980s to 2019) reporting PAH concentrations in sediments of the Mediterranean Sea. Subsequently, the collected data were spatialised and clustered according to the four basins of the Mediterranean as defined by the Mediterranean Strategy on Sustainable Development and the United Nations Environment Programme Mediterranean Action Plan. We employed additive models, a flexible and versatile tool for coping with non-linear trends by means of smooth functions, to estimate temporal trends in PAH concentrations. Finally, the primary origins of contamination and temporal trends in ecological risk were determined using a combination of approaches. The results indicated that PAHs in Mediterranean sediments originate primarily from biomass burning, with a contribution from combustion of coal and liquid fossil fuels, the latter being representative of sites near urban centres or harbours. A significant positive correlation between annual growth rates of PAH concentration in sediment and wildfires was found. The estimated non-linear trends of concentrations and risk showed different temporal patterns across basins. In recent years, especially in the Western Mediterranean, the estimated trends suggest PAH concentrations are posing an increasing risk. These results indicate the need for stronger efforts to achieve the objectives of the Marine Strategy Framework Directive.

## 1. Introduction

The Mediterranean Sea is one of the most highly valued marine and coastal environments. However, it is also one of the most vulnerable in the world due to the multiple pressures of anthropic activities along its coastline (EEA, 2015). Since the early 90's, several directives have been adopted by stakeholders for the protection of this environment (details in [Supplementary Material – SI](#)).

It is well known that sediments may accumulate large quantities of contaminants (Bouloubassi and Salot, 1993), which can negatively affect benthic organisms and indirectly disrupt the functionality of marine ecosystems (Zheng et al., 2016; Honda and Suzuki, 2020). Furthermore, as benthic organisms are an important food source for

other organisms, the contaminants they assimilate from sediments can be transferred throughout the trophic chain (Lyytikäinen et al., 2007). In this framework, the Environmental Quality Standards Directive 2008/105/EC (EQSD) has been a very important step in the use of sediments and biota as matrices for chemical status assessment under the Water Framework Directive 2000/60/EC. The EQSD laid down the Environmental Quality Standards (EQS) at the European Community level for 33 'priority substances' and eight 'other pollutants'. EQS are defined as the concentration of a particular substance or group of substances in water, sediment, or biota that should not be exceeded to protect human health and the environment. For the majority of priority substances, the EQSD defined the EQS for the water column; however, for sediment and biota, the EQSD allowed Member States to establish their own EQS at the

\* Corresponding author.

E-mail address: [sara.villa@unimib.it](mailto:sara.villa@unimib.it) (S. Villa).

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national level for priority substances with significant potential to accumulate. More recently, Directive 2013/39/EU has established EQS for priority substances in waters biota and sediments, including for the concentration in sediments of several polycyclic aromatic hydrocarbon (PAH) compounds: anthracene, fluoranthene, naphthalene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene.

PAHs are of particular concern given their ubiquity in various environmental compartments and their potentially harmful effects on ecosystems. PAHs are derived mainly from anthropogenic sources because of incomplete combustion of coal, wood, or gasoline, as well as industrial processes (Lipiatou and Saliot, 1991; Yunker et al., 2002). However, they can also be emitted from natural sources, including forest fires, volcanic activity, and microorganisms, contributing to background contamination in the environment (Budzinski et al., 1997). PAHs can be transported over long distances and can enter the aquatic environment via atmospheric pathways after dry or wet deposition processes (Ferrero et al., 2019) or be released directly into water bodies via transport or industrial use of oil, industrial wastewater, or urban runoff (Hatzianestis et al., 2020). The affinity of individual compounds for organic matter is determined by physicochemical parameters such as the organic carbon/water partition coefficient (Koc), which is high for PAHs.

PAHs are highly persistent. They show moderate to low solubility in water, which promotes adsorption to particulate matter and subsequent build-up in sediments; thus, sediments act as PAH sinks (Law et al., 1997). Furthermore, thanks to their liposolubility, which allows them to cross cell membranes and penetrate and settle into adipose tissues, they can accumulate in aquatic organisms and food chains (Neroda et al., 2019). Some PAHs are known to have carcinogenic, mutagenic, and teratogenic properties. Consequently, 16 PAHs have been evaluated as priority hazardous substances by the United States Environmental Protection Agency. Moreover, PAHs have been classified as ubiquitous persistent, bioaccumulative, and toxic compounds under the EU Water Framework Directive (2013/39/EU). In addition to mutagenic and carcinogenic effects, recent toxicological studies have revealed the potential of PAHs to cause oxidative stress and genotoxicity and to act as endocrine disruptors (Honda and Suzuki, 2020).

In this context, the present study aimed to increase knowledge of the ecological quality of benthic environments in the Mediterranean Sea with reference to the goals of the Mediterranean Action Plan (UNEP/MAP) and Barcelona Convention (available at <https://www.unenvironment.org/unepmap/who-we-are/barcelona-convention-and-protocols>). In particular, our study aimed (i) to reconstruct spatial and temporal trends in the risk posed by PAHs to benthic communities in Mediterranean sediments and (ii) to identify the prevalent sources of PAH contamination in the Mediterranean Sea. This was done through multiple steps, starting with an in-depth literature survey of over 40 years of studies reporting the presence of PAHs in sediments of the Mediterranean Sea. The collected data were organised into a database and then spatialised according to the four basins of the Mediterranean as defined by MSFD and UNEP/MAP. Subsequently, temporal trends in sedimentary PAH contamination were estimated for each of the four basins through the application of additive statistical models. Finally, the prevalent origins of contamination and the temporal trend in risk were determined using a combination of various approaches.

## 2. Materials and methods

### 2.1. Study area and literature survey

Published data on PAH concentrations in sediments of the Mediterranean Sea basin were collected from scientific journals. Articles were found by searching Google Scholar, websites of publishing houses (such

as ScienceDirect, Elsevier, Wiley, and Springer), and CuriousOne (the search service of the University of Milano-Bicocca).

The available literature was searched by running a simple search string consisting of specific keywords along with Boolean operators and a wildcard symbol (\*). Further details on the string-searching algorithm are reported in SI. Only articles verified as peer-reviewed were selected for the study. Fifty-five papers that reported the summed concentration of PAHs as a group were excluded from the database, as this work was focused on the risk characterisation of individual PAHs.

Each sediment sample was treated as an individual entry in the database. Details such as the year of collection and geographical coordinates were also included. In past years, several schemes have been proposed for compartmentalising the Mediterranean Sea to better understand ecological processes at different spatial scales and to facilitate ecosystem management. We followed the MSFD and UNEP/MAP scheme, which divides the Mediterranean Sea into four basins. These basins are somewhat homogeneous in ecological community composition and environmental conditions and are therefore appropriate units for spatial management at a regional scale. They often cross political boundaries, highlighting the need for intergovernmental cooperation. Based on their geographic coordinates, the samples were clustered according to the four basins defined by MSFD and UNEP/MAP: the Western Mediterranean basin (Balearic Islands, Gulf of Lion, Sea of Sardinia, Tyrrhenian Sea), the Adriatic Sea basin, the Central Mediterranean basin (Central Mediterranean and Ionian Sea), and the Aegean–Levantine basin (Fig. S1).

The period investigated spanned approximately 40 years (from the early 1980s to 2019). Data were collected both from locations influenced by anthropogenic activities, such as industrial areas, megacities, and harbours, and from areas not highly impacted by anthropogenic pressure. Concentrations of PAHs are given in ng/g dry weight (d.w.). Each concentration value in the dataset is given as the mean calculated or reported by the original authors, together with the standard deviation and the number of observations for each sampling site.

We focused on the 16 PAHs considered priority substances, which can be grouped according to their number of aromatic rings, as follows:

- Two rings: naphthalene (Nap)
- Three rings: acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phen), anthracene (Ant)
- Four rings: fluoranthene (Fl), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr)
- Five rings: benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DBahA)
- Six rings: indeno[1,2,3-cd]pyrene (IP), benzo[ghi]perylene (BghiP)

The entire dataset is given in Table S1, with the collected data grouped according to the four basins. All additional figures and tables are provided in SI.

### 2.2. Sources of variability and uncertainty

We assumed that data from different literature sources were comparable across space and time. However, differences among studies, such as variations in sampling, analytical procedures and differences in study scope, necessarily increased the variability and uncertainty in the data collected. Moreover, the use of sediment samples to assess temporal trends in pollution is also prone to variability and misinterpretation, as the thickness of the sampled layer is a function of the sedimentation rate, which can influence the concentration of pollutants. Sedimentation rate varies by sampling area, and the characteristics of the layer sampled depend on the sedimentation rate in each area, further increasing variability. However, other authors have discussed the uncertainty

associated with the use of surface sediments in the historical reconstruction of pollution (Gómez-Gutiérrez et al., 2007; Merhaby et al., 2020) and concluded that this matrix is suitable for reconstructing temporal trends (Picer and Piccer, 1995). Additional uncertainty could arise from the fact that the number of data points available for the different areas of the Mediterranean Sea varies in time and space. These sources of uncertainty may affect our capability to characterise the impact of PAHs in these areas over the decades.

We are aware that the uncertainty and variability in our collected data cannot be disregarded. Nevertheless, this study is not intended to accurately describe PAH distribution in the Mediterranean Sea, but rather to evaluate the risk that PAHs may pose to sediment-dwelling organisms in the region.

### 2.3. Statistical analysis

Temporal trends in PAH concentrations differ considerably between the four basins of the Mediterranean because of site characteristics and several sources of variability, making it necessary to use a flexible and versatile statistical tool to describe non-linear relationships. Therefore, we used additive models to estimate temporal trends in PAH concentrations. Additive models can reveal complex structures in the data that would otherwise be lost.

We considered smoothing spline regression models of the form

$$\log(y_i) = \alpha + f(\text{Time}_i, \beta) + \epsilon_i, \quad \epsilon_i \sim N(0, \sigma^2), \quad (i = 1, \dots, n), \quad (1)$$

where  $n$  is the sample size;  $\alpha$  is the model intercept, that is, the mean value of the response;  $\log(y_i)$ ,  $f(\cdot)$  is a spline function of a time variable and represents the trend in the response; and  $\epsilon_i$  are the model residuals, assumed to be Gaussian-distributed with mean 0 and constant variance  $\sigma^2$ . A log base 10 transformation was applied to the concentration values to overcome the skewness in the data and to meet the underlying assumptions of normality.

Smoothing spline regression models can be thought of as penalised least-squares regression models. The maximisation of the penalised spline regression function implies a trade-off between smoothness and model fit, which is controlled by a tuning parameter  $\lambda \geq 0$ . Among all functions  $f$  with two continuous derivatives, the model aims to find the one that minimises the penalised residual sum of squares (RSS).

$$RSS(f, \lambda) = \sum_{i=1}^n (\log(y_i) - \alpha - f(\text{Time}_i, \beta))^2 + \lambda \int f''(t)^2 dt \quad (2)$$

The penalty  $\int f''(t)^2 dt$  expresses the degree of curvature of a spline function  $f$  in terms of the second derivative of  $f$ . For a given  $\lambda$ , the solution of (2) is unique, taking the form of a natural cubic spline with knots at the values  $x_i (i = 1, \dots, n)$  (Wood, 2004).

To explore the relationship between sediment concentrations and fire activity trends, we used temporal cross-correlations, as a suitable indicator of similarity between the two series observed at different times. For the fire trend we have considered the fire weather index (FWI) computed by Giannaros and co-workers (Giannaros et al., 2021), used as indicator of fire danger in the Mediterranean area. In particular we examined three FWI-based indices, namely seasonal count of days with FWI > 30 (FWI30), and seasonal 50th and 90th percentile of FWI (FWIp50 and FWIp90), which provide a realistic representation of the climatic conditions susceptible for spreading fires. FWI data for 30 years (1987–2016) where downloaded from Zenodo platform (Giannaros et al., 2020).

As reported by Gonçalves and Sousa (2017), the statistics of forest fires in the Mediterranean basin countries had started in different times; firstly in the '80 s for France, Greece, Italy, Portugal, and Spain, in the '90 s for Croatia, Morocco, and Turkey, in the 2000 s for Cyprus and Slovenia, and lastly for Algeria and the former Yugoslav republic of Macedonia and Lebanon around 2010 s. Up to now no data are available for Albania, Egypt, Israel, Libya, Montenegro, Syria, and Tunisia. Hence, we focused the cross-correlation analysis on the Western Mediterranean

Basin only, for which the longest time series is available.

We studied the cross (lagged) correlations between the three FWI-based indices and the first-time difference of the predicted levels of log-concentrations, obtained from the fitted additive models, estimated using the series of the weighted mean values for each year of observations. For each year (from May to September), in the considered temporal window, we computed the median values of each index over all coordinate points belonging to the South-East Euro-Mediterranean area.

Furthermore, to avoid spurious relationships, ascribable to autocorrelation, and to make the series stationary, we considered the first difference transformation of the log-concentrations, defined as  $DIFF(\log(y_t)) = \log(y_t) - \log(y_{t-1}) = \log(y_t/y_{t-1})$ , where  $\log(y_t)$  denotes the value of the time series of log-concentrations at time  $t$ , ( $t = 1, \dots, T$ ). This transformation has an advantage in terms of interpretation, as  $DIFF(\log(y_t))$  represents the annual growth rate of concentration levels. Note that cross-correlation does not infer causation, such as whether there are likely causal relationships between the series, nevertheless correlational evidence may be useful for prediction.

Lastly, to look at an overall measure of presence of serial correlation between the two mentioned series, a Ljung–Box test (Ljung and Box, 1978) was used. The test statistic is:

$$Q = T(T+2) \sum_{k=1}^h \frac{\hat{\rho}_k^2}{T-k}$$

where  $T$  is the temporal series length,  $\hat{\rho}_k$  is the sample cross-correlation at lag  $k$ , and  $h$  is the number of lags being tested. Under the null of independence, namely all cross-correlation coefficients are simultaneously equal to zero, the  $Q$  statistic asymptotically follows a  $\chi_h^2$ , since the limiting distribution of  $(\rho_1, \dots, \rho_h)$  is multivariate normal with mean vector zero.

All statistical analyses were performed in R statistical software using the mgcv package for additive model estimates (Wood, 2017).

### 2.4. PAH diagnostic ratios

PAH diagnostic ratios are frequently used to identify contamination sources. The approach is based on the hypothesis that PAH isomers have the same physicochemical properties and therefore undergo transformation and degradation processes at the same rate, maintaining the ratio found in the emission source (Biache et al., 2014). Although this method is subject to uncertainties owing to differences in water solubility, adsorption, and volatility between PAHs of the same molecular weight (Dvorská et al., 2011), several studies have confirmed the suitability of PAH diagnostic ratios in source identification (Yunker et al., 2002; Wang et al., 2010; Jiang et al., 2011).

In the present study, the following PAH ratios were calculated:

- Fluoranthene/(fluoranthene + pyrene) [Fl/(Fl + Pyr)]
- Anthracene/(anthracene + phenanthrene) [Ant/(Ant + Phen)]
- Benz[a]anthracene/(benz[a]anthracene + chrysene) [BaA/(BaA + Chr)]
- Indeno [1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene + benzo[ghi]perylene) [IP/(IP + BghiP)]

### 2.5. Ecological risk classification

Since the 1980s, various sediment quality guidelines (SQGs) have been proposed for use in assessing sediment quality in terms of the concentration of contaminants that can cause adverse effects on benthic communities (Ingersoll and Wenning, 2002). Generally, these approaches are based on empirical or theoretical relationships (Burton and Allen, 2002). In our study, we used two empirical approaches: the effects range median (ERM) (Long et al., 1995, 2006) and the probable effects level (PEL). Both approaches are very simple methods of predicting the

probability that contaminants will have effects on benthic organisms. The ERM and PEL values for the PAHs considered in this study, as proposed by Long et al. (1995) and MacDonald et al. (1996), are given in Table S2 (expressed in ng/g d.w.).

We applied both ERM and PEL to classify the hazard posed by each PAH. The concentration of each individual compound (*i*) in the dataset was divided by its SQG value (ERM or PEL). The resulting quotient ( $ERMq_i$  or  $PELq_i$ ) was classified as indicating one of four hazard levels, as proposed by Cardellicchio et al. (2007):

- Low hazard ( $ERMq_i < 0.1$ ,  $PELq_i < 0.1$ )
- Medium-low hazard ( $ERMq_i = 0.11-0.5$ ,  $PELq_i = 0.11-1.5$ )
- Medium-high hazard ( $ERMq_i = 0.51-1.5$ ,  $PELq_i = 1.51-2.3$ )
- High hazard ( $ERMq_i > 1.5$ ,  $PELq_i > 2.3$ )

Moreover, to obtain a deeper insight into the temporal trend of risk in the four basins, we also applied the risk quotient (RQ) approach for concentrations of the eight PAHs for which EQS for sediments (given as an average annual value in ng/g d.w.) are available (Directive 2013/39/EU) (Table S2). We calculated the average annual concentrations (AA\_conc) of these PAHs and compared them to the available EQS ( $RQ = AA\_conc/AA\_EQS$ ). When the RQ was below 1, the risk was considered acceptable, whereas if RQ was  $> 1$ , the risk was considered unacceptable.

### 3. Results and discussion

#### 3.1. Geographical scope of the data

All data collected are given in Table S1. Specifically, 31 studies were conducted in the Western Mediterranean, 22 in the Adriatic, 14 in the Central Mediterranean, and 22 in the Aegean-Levantine basin. Each paper reported multiple observations. For the Western Mediterranean, up to 65 average values for the single PAHs were reported based on 777 observations. For the Adriatic, the corresponding numbers were 55 and 858; for the Central Mediterranean, 30 and 236; and for the Aegean-Levantine basin, 56 and 571. These numbers confirm that, as stated by Nikolaou et al. (2009), most studies of the Mediterranean Sea are focused on the north-western area, whereas data are scarce for the eastern and southern Mediterranean.

#### 3.2. Spatial variability of PAH concentrations in the four Mediterranean Sea basins

Descriptive statistics for the log10-transformed PAH concentrations for each basin are reported in Table 1, along with the temporal window (period), and the total number of years with at least one observation (J). As a measure of location, we reported the arithmetic mean and the median, which is robust against outliers. As a measure of scale, we considered the standard deviation (sd) and its robust counterpart, the median absolute deviation (MAD).

We adopted the logarithmic transformation of the original concentrations for each single compound to address right skewness in the data. In case of multiple observations for the same year, we calculated the arithmetic mean of the log10-concentrations, weighted as a function of the number of observations. Finally, we combined the weighted averages, related to the several years of observations, computing the overall mean and median concentration values (see Table 1), which may be considered as the feasible concentrations in benthic sediments in the Mediterranean basin for the selected temporal window. Moreover, the reported measures of variation, i.e. sd and MAD, suggest that such summary measures are in general quite stable.

Following the classification of pollution levels proposed by Baumard et al. (1998), the combined concentration of the 16 PAHs considered in this study, which are computed as the sum of the location measures for each compound back-transformed in the original scale (ng/g d.w.), for

**Table 1** Descriptive statistics for the log10-PAH concentrations in sediments from the four Mediterranean basins (ng/g d.w.).

	Mediterranean basins (ng/g d.w.)															
	ALS	CMS	AS	WMS	Flu	Phen	Ant	Fl	Pyr	BaA	Chr	BbF	BkF	DBaH	IP	BghIP
mad	0.47	0.63	0.52	0.5	0.35	0.72	0.66	0.43	0.31	0.83	0.98	0.49	0.35	0.92	0.78	0.99
sd	0.52	0.51	0.84	0.84	0.58	0.49	0.91	0.61	0.5	0.69	0.76	0.65	0.46	0.83	0.64	0.85
median	1.25	1.13	0.94	0.94	0.97	1.22	0.85	1.24	1.39	1	1.28	1.05	0.87	1.32	1.42	1.19
mean	1.22	1.15	1.12	1.12	0.75	1.19	0.77	1.21	1.3	1.02	1.28	1.11	0.8	1.38	1.27	1.29
J	11	9	9	11	12	13	14	14	14	12	11	12	11	13	13	13
period	1999-2019	1999-2019	1999-2019	1999-2019	1999-2019	1994-2019	1994-2019	1994-2019	1994-2019	1994-2019	1999-2019	1999-2019	1999-2019	1994-2019	1994-2019	1994-2019
mad	0.35	0.69	0.87	0.87	0.9	0.89	0.85	0.91	0.86	0.59	0.9	1.21	0.84	1.13	1.35	1.11
sd	0.47	0.9	0.76	0.76	0.71	0.74	0.76	0.73	0.75	1.04	0.92	1.04	0.97	1.09	1.01	0.9
median	1.01	0.82	0.57	0.57	0.95	1.55	1.02	1.9	2.17	0.78	2.02	1.23	1.78	1.77	1.17	1.58
mean	0.96	0.77	0.71	0.71	0.92	1.77	1.26	1.97	1.97	1.38	1.86	1.62	1.53	1.52	1.14	1.53
J	8	5	7	7	7	10	10	10	10	10	9	7	9	10	8	9
period	2001-2014	2001-2014	2001-2014	2001-2014	2001-2014	1999-2014	1999-2014	1999-2014	1999-2014	1999-2014	2001-2014	2001-2014	2001-2014	1999-2014	2001-2014	1999-2014
mad	0.72	0.62	0.62	0.62	0.88	0.21	0.31	0.34	0.42	0.51	0.36	0.42	0.39	0.38	0.36	0.17
sd	0.89	0.99	0.76	0.76	0.9	0.61	0.78	0.67	0.62	0.76	0.72	0.69	0.74	0.81	0.67	0.6
median	0.71	-0.06	0.21	0.21	0.54	1.3	0.76	1.63	1.53	1.41	1.39	1.59	1.26	1.26	0.53	1.32
mean	0.65	0.15	0.16	0.16	0.49	1.41	0.88	1.75	1.69	1.48	1.54	1.7	1.39	1.37	0.73	1.37
J	11	9	11	11	13	13	14	13	13	13	14	13	13	14	13	12
period	1983-2014	1983-2014	1983-2014	1983-2014	1983-2014	1983-2014	1983-2014	1983-2014	1983-2014	1983-2014	1983-2014	1990-2014	1990-2014	1983-2014	1990-2014	1990-2014
mad	0.74	0.32	0.87	0.87	0.51	0.64	0.82	0.88	0.94	0.91	0.73	0.92	0.7	0.84	0.79	0.78
sd	1.08	1.2	1.1	1.1	1.1	0.98	1.04	1.02	1.03	1.01	1.04	1.06	0.93	1	0.89	0.95
median	1.31	1	1.13	1.13	1.22	2.25	1.26	2.28	2.22	1.91	2.05	2.09	1.77	1.95	1.65	1.84
mean	1.45	1.47	1.25	1.25	1.41	2.2	1.42	2.23	2.16	1.88	2.04	2.05	1.8	1.96	1.75	1.89
J	13	9	12	12	12	19	19	20	20	20	16	18	18	20	14	19
period	1999-2017	1999-2017	1999-2017	1999-2017	1999-2017	1985-2017	1985-2017	1985-2017	1985-2017	1985-2017	1987-2017	1985-2017	1985-2017	1985-2017	1987-2017	1985-2017
compound	Nap	Acy	Acc	Acc	Flu	Phen	Ant	Fl	Pyr	BaA	Chr	BbF	BkF	DBaH	IP	BghIP

ease of interpretation purposes, fell within the moderate range in the Adriatic Sea basin (mean: 370 ng/g d.w.; median: 284 ng/g d.w.), the Central Mediterranean basin (mean: 571 ng/g d.w.; median: 615 ng/g d.w.), and the Aegean–Levantine basin (mean: 225 ng/g d.w.; median: 231 ng/g d.w.), whereas in the Western Mediterranean basin (mean: 1279 ng/g d.w.; median: 1265 ng/g d.w.), the pollution level could be classified as moderate to high.

The Western Mediterranean displayed the highest total PAHs concentration of all four basins. This could be due to artefacts resulting from selection of sampling areas in proximity to industries, harbours, and urban centres, or to the effects of environmental factors that drive the fate of these contaminants. For example, studies in the port of Naples reported high PAH concentrations of 3140 ng/g (Sprovieri et al., 2007) and 2796 ng/g (Feo et al., 2011), whereas PAH levels up to 50 µg/g were reported in Toulon harbour (Benlahcen et al., 1997). Aside from industrial activity, riverine input is another important factor in the transition of PAHs to the Mediterranean basin. In France, at the mouth of the Rhône River, PAH values ranged from 3437 to 9324 ng/g in 1985 and from 2098 to 3657 ng/g in 1986 (Bouloubassi and Saliot, 1993), whereas in 1987, they ranged from 2421 to 3182 ng/g (Lipiatou and Saliot, 1991). In Italy, Montuori and Triassi (2012) recorded PAH values of 352 ng/g at the mouth of the Sarno River, known as ‘the most polluted river in Europe’.

The relative abundance of PAHs (Fig. 1), calculated as the ratio of the concentration of each individual PAH to the total concentration of PAHs, showed similar patterns in the Western Mediterranean, Adriatic Sea, and Central Mediterranean. The most abundant PAHs in the Western Mediterranean basin were Fl (13%), Phen (12%), and Pyr (11%). Fl was the most prevalent PAH in the Adriatic Sea basin, with an abundance of 15%, followed by BbF and Pyr, which accounted for 14% and 13%, respectively. Similarly, the abundance pattern of PAHs in the Central Mediterranean basin was characterised by the prevalence of Fl and Pyr (16%), Chr (13%), and Phen (10%). In contrast, the Aegean–Levantine basin was characterised by a slightly different abundance pattern, with BaP as the most abundant PAH (11%), followed by Pyr and BghiP (9%).

The relative abundance patterns observed in this study are consistent with those reported by other authors in sediments worldwide. Simpson et al. (1996) reported that PAHs of high molecular weight (especially Fl, Pyr, BbF, BjF, BkF, BaP, and BeP) were dominant in marine sediments from Kitimat Harbor, Canada. Hassan et al. (2018) reported that PAHs with two to four rings accounted for the majority of PAHs in surface sediments from Qatar, except for some samples in which five-ring PAHs dominated. Differing abundance patterns in the Barents Sea were highlighted by Dahle et al. (2006), with Fl and Pyr as the dominant PAHs in sediments from Kola and Pechenga Bays, whereas alkylated homologues of Nap and Phen/Ant dominated among the PAHs present in the inshore area of Svalbard.

### 3.3. Estimated temporal trends in PAH concentrations

Fig. 2 provides a comprehensive picture of estimated temporal trends in PAH concentration (solid black lines), accompanied by 95% pointwise confidence intervals (grey shaded areas). The concentrations of almost all the considered PAHs showed a non-linear trend, well captured by smooth functions, throughout the study period across the four basins of the Mediterranean Sea, with substantial differences among areas (Fig. 2 and S2–S4; Tables 2 and Tables S3–S5).

Table 2 gives the approximate significance of the smooth terms in the additive models (see Eq. (1)) used to estimate temporal trends in the Western Mediterranean basin. The average explained deviance was 24%; that is, 24% of the total sum of squares was explained by the model (see Eq. (2)). The smoothing term, tested by F-test, was significant at the 5% level for all analysed compounds, with the sole exception of Flu ( $p = 0.08$ ). The estimated degrees of freedom (edf) suggest a significant and highly non-linear temporal trend for 11 out of 16 compounds. According to Zurr et al. (2009), 1 edf is equivalent to a linear relationship, an edf between 1 and 2 suggests a weakly non-linear relationship, and an edf > 2 indicates a highly non-linear relationship.

The estimated trend for the Western Mediterranean basin is clearly non-linear and shows a U-shaped pattern for almost all PAHs. At the beginning of the period considered in this study, the concentrations were quite high for almost all the PAHs. After an initial decrease in concentrations in the late 1980 s, values oscillated, showing a new increase after the year 2005.

In the Adriatic Sea, most PAHs showed an increasing trend, generally at the 5% level of significance, with one (IP) showing a 10% level of significance (Table S3 and Fig. S2). In contrast, Phen, BaA, Chr, DBahA, and BghiP did not show significant trends.

In the Central Mediterranean, most PAHs showed an increasing trend during the period considered (Table S4 and Fig. S3). This was significant for the majority of the compounds ( $p < 0.05$ ), but less significant for Ant, BaA, and Chr ( $p < 0.1$ ). Concentrations increased from 1990 to 2000, then slightly decreased before rising again more recently. In contrast, Nap, Acy, and BaA did not show significant trends during the time period considered.

For the Aegean–Levantine basin, log concentrations smoothed by the additive models displayed the lowest edf compared with other basins. Only four PAHs showed increasing trends at the 5% level of significance (Acy, Ant, BaP, and DBahA), and one PAH showed an increasing trend at the 10% level of significance (BbF). No significant trends were found for the other compounds investigated.

These results clearly indicate that the Western Mediterranean is the area experiencing the most significant decreases and increases, with a new rise in PAH concentrations beginning around 2005. These findings are consistent with the possible emission of PAHs from forest fires. In

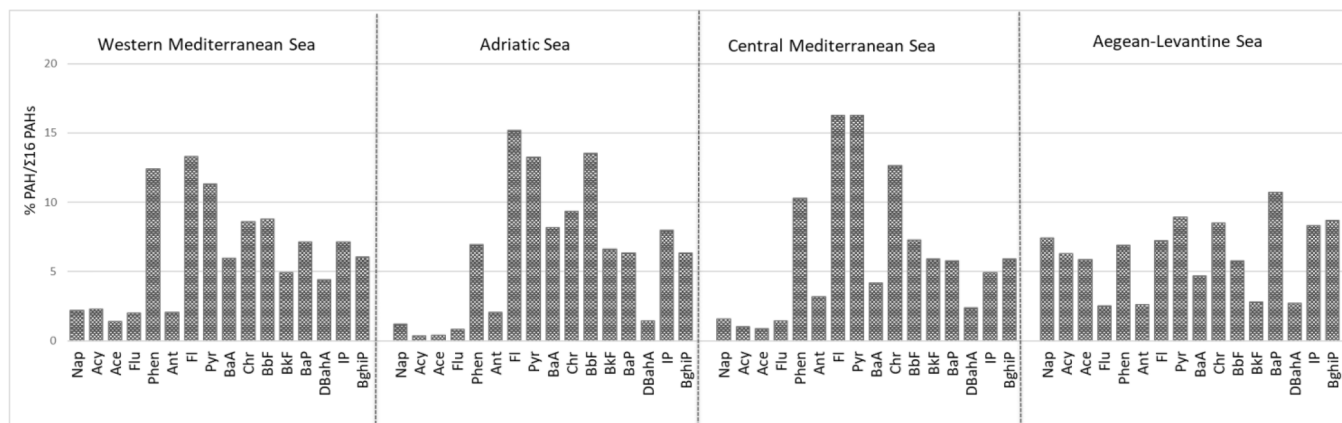


Fig. 1. Relative abundance patterns of 16 PAHs in the four basins of the Mediterranean.

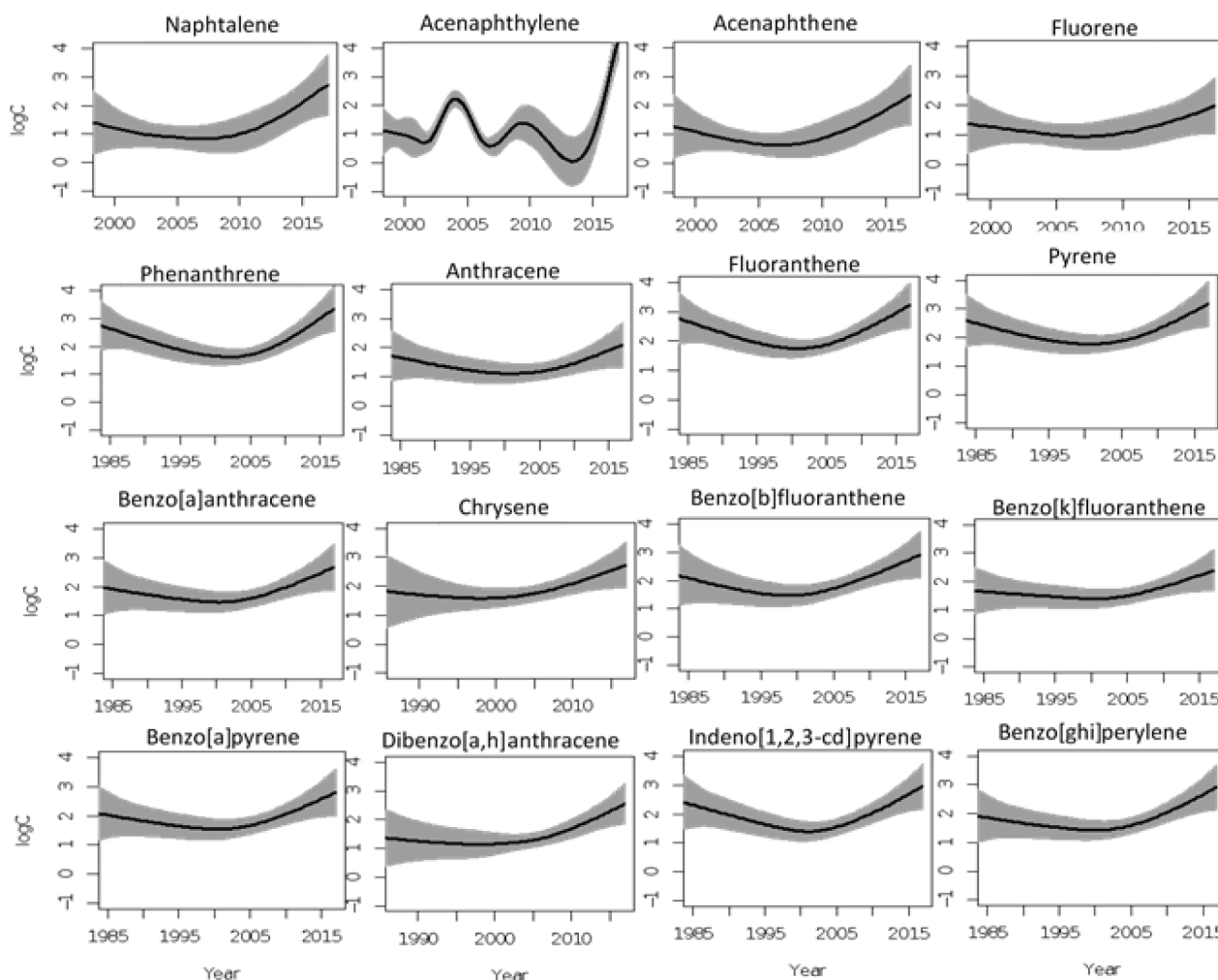


Fig. 2. Fitted smooth functions of time (trends, solid black lines) and approximate 95% pointwise confidence intervals (grey shaded areas) for analysed PAHs from the Western Mediterranean basin.

Table 2

Summary of additive model used to estimate temporal trend for Western Mediterranean basins. The estimated degrees of freedom for the smoothing term (edf), its significance (p-value) tested by F test, and the proportion of the null deviance explained by the model are reported.

Substances	edf	p-value	Deviance explained
Naphthalene	2.276	0.006	0.312
Acenaphthylene	7.218	0	0.897
Acenaphthene	2.156	0.008	0.258
Fluorene	1.6	0.08	0.135
Phenanthrene	2.506	0	0.254
Anthracene	1.572	0.032	0.101
Fluoranthene	2.223	0.001	0.203
Pyrene	2.178	0.003	0.175
Benzo[a]anthracene	1.971	0.016	0.137
Chrysene	1.757	0.015	0.133
Benzo[b]fluoranthene	2.051	0.004	0.192
Benzo[k]fluoranthene	1.868	0.031	0.126
Benzo[a]pyrene	2.031	0.012	0.148
Dibenzo[a,h]anthracene	2.148	0.002	0.271
Indeno[1,2,3-cd]pyrene	2.291	0.001	0.227
Benzo[ghi]perylene	2.32	0.002	0.204

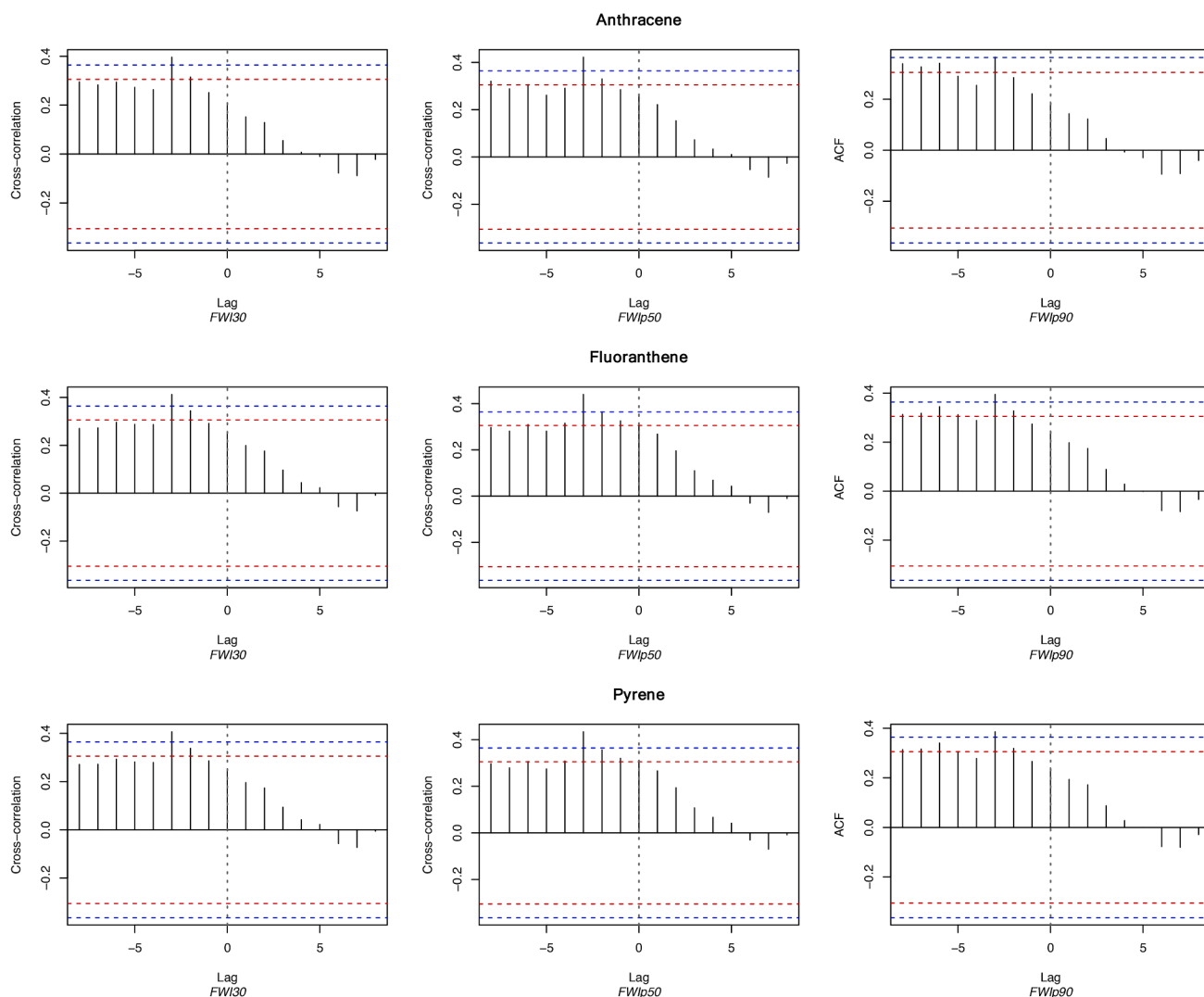
this area, extreme fire weather conditions became more frequent during the thirty-year period from 1987 to 2016, particularly in the Iberian Peninsula (Giannaros et al., 2021). An increase in forest fire events was also reported by Rodrigues et al. (2013), who recorded a rise in the

number of fires and burned areas in this region over the previous 25 years, especially in Portugal, Spain, and Sicily. In contrast, in the south-eastern Mediterranean, Rodrigues et al. (2013) reported a decreasing trend in the number of fires, which was correlated with a relatively stable temporal trend in PAH concentrations in this area.

The relationship between levels of PAHs concentrations and fire activity was explored by means of cross-correlations as described in Section 2.3. Fig. 3 reports the cross-correlation functions of the current change in annual growth rate of log-concentration of Ant (top panel) and time lag (expressed in years) of the three FWI-based indices, that are seasonal count of days with FWI > 30 (FWI30), and seasonal 50th and 90th percentile of FWI (FWIp50 and FWIp90).

The most dominant cross-correlations occur at the time lag of 3 years; we could argue that annual growth rate of concentration level is relatively high 3 years after high fire activity (significant correlation at time lag of 3 at level 95%). Also, at the time lag of 2 years, we begin to observe a positive correlation, significant at level 90%. Similar considerations may also apply to fluoranthene (mid panel) and pyrene (bottom panel) compounds, as well as for the other contaminants analysed in this study. A 3 years lag between the occurrence of fire events and the rising of PAH concentrations in marine sediments is a plausible time considering all the environmental processes involved in the distribution and final deposition in sediment of these molecules.

The Ljung-Box tests detected the presence of cross-correlation up to lag 8 between annual growth rate of concentration level and each FWI-



**Fig. 3.** Cross-correlation functions (vertical lines) of the current change in annual growth rate of log-concentration and time lag (in years) of the three FWI-based indices: FWI30, FWIp50, and FWIp90. The dotted grey vertical lines denote lag 0. The dotted blue (red) horizontal lines represent 95% (90%) confidence intervals (Top to bottom: anthracene, fluoranthene, pyrene, respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 3**

Ljung-Box Q-Statistics, corresponding p-values, and Holm–Bonferroni’s adjusted p-values (adj. p-value) for each compound.

compound	FWI30			FWI50			FWI90		
	Q-stat	p-value	adj.p-value	Q-stat	p-value	adj.p-value	Q-stat	p-value	adj.p-value
Naphtalene	17.881	0.037	0.037	20.132	0.017	0.017	18.651	0.017	0.017
Acenaphthylene	23.029	0.006	0.012	25.707	0.002	0.005	23.99	0.002	0.005
Acenaphthene	26.928	0.001	0.006	29.961	0.000	0.002	28.181	0.000	0.002
Fluorene	24.321	0.004	0.011	27.073	0.001	0.004	25.365	0.001	0.004
Phenanthrene	28.109	0.001	0.005	32.204	0.000	0.001	29.916	0.000	0.001
Anthracene	27.692	0.001	0.005	31.557	0.000	0.001	29.311	0.000	0.001
Fluoranthene	30.202	0.000	0.004	34.662	0.000	0.001	32.202	0.000	0.001
Pyrene	29.339	0.001	0.004	33.728	0.000	0.001	31.277	0.000	0.001
Benzo[a]anthracene	30.223	0.000	0.004	34.527	0.000	0.001	32.174	0.000	0.001
Chrysene	31.275	0.000	0.004	36.022	0.000	0.001	33.506	0.000	0.001
Benzo[b]fluoranthene	29.694	0.000	0.004	34.574	0.000	0.001	31.975	0.000	0.001
Benzo[k]fluoranthene	31.278	0.000	0.004	350.582	0.000	0.001	33.229	0.000	0.001
Benzo[a]pyrene	30.733	0.000	0.004	35.117	0.000	0.001	32.747	0.000	0.001
Dibenz[a,h]anthracene	31.405	0.000	0.004	35.628	0.000	0.001	33.346	0.000	0.001
Indeno[1,2,3cd]pyrene	30.982	0.000	0.004	35.541	0.000	0.001	33.029	0.000	0.001
Benzo[ghi]perylene	39.543	0.001	0.004	34.041	0.000	0.001	31.535	0.000	0.001

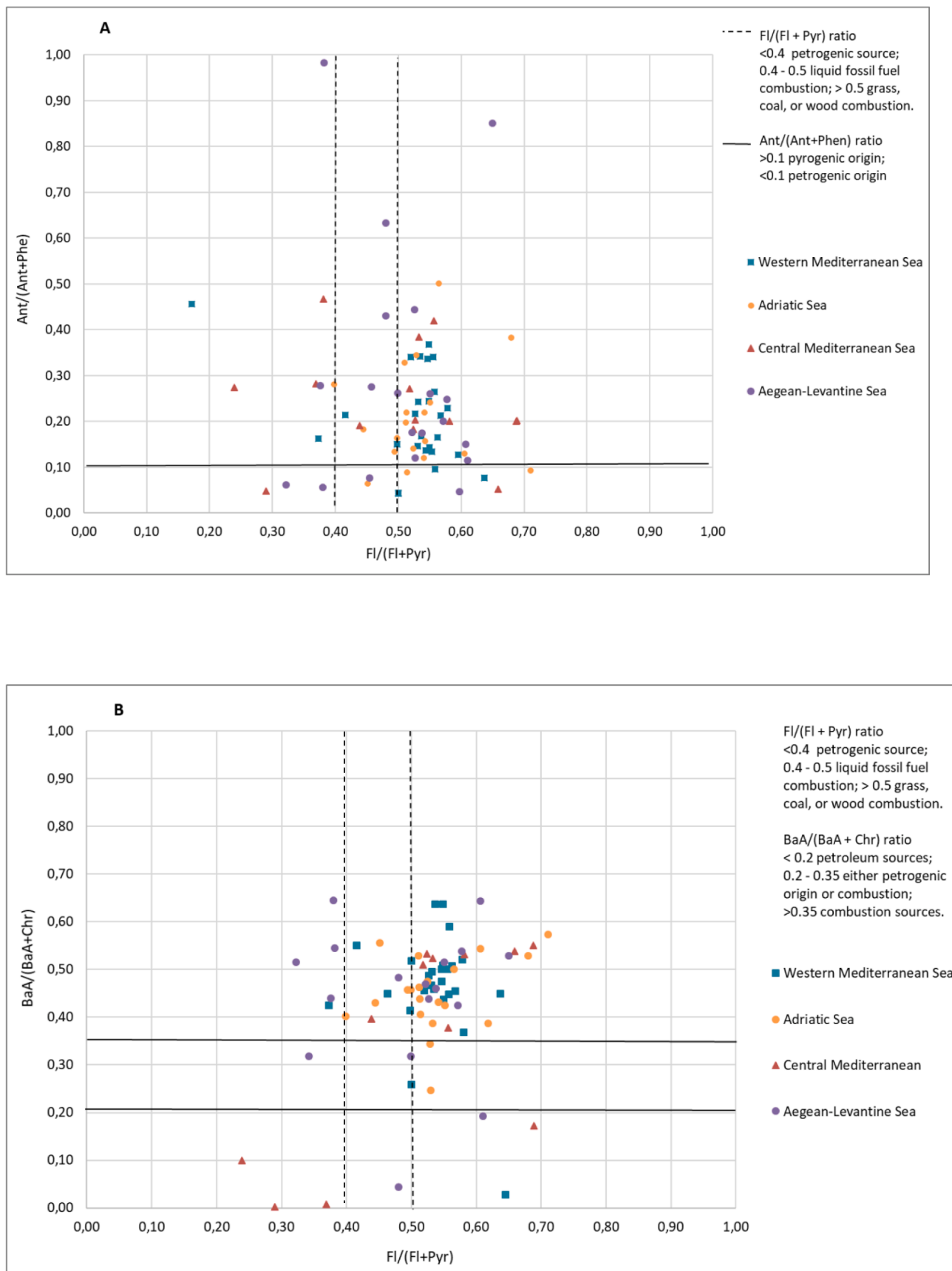


Fig. 4. Diagnostic ratios applied for identification of PAH pollution sources. A) Ant/(Ant + Phe) vs Fl/(Fl + Pyr); B) BaA/(BaA + Chr) vs Fl/(Fl + Pyr); C) IP/(IP + BghiP) vs Fl/(Fl + Pyr).



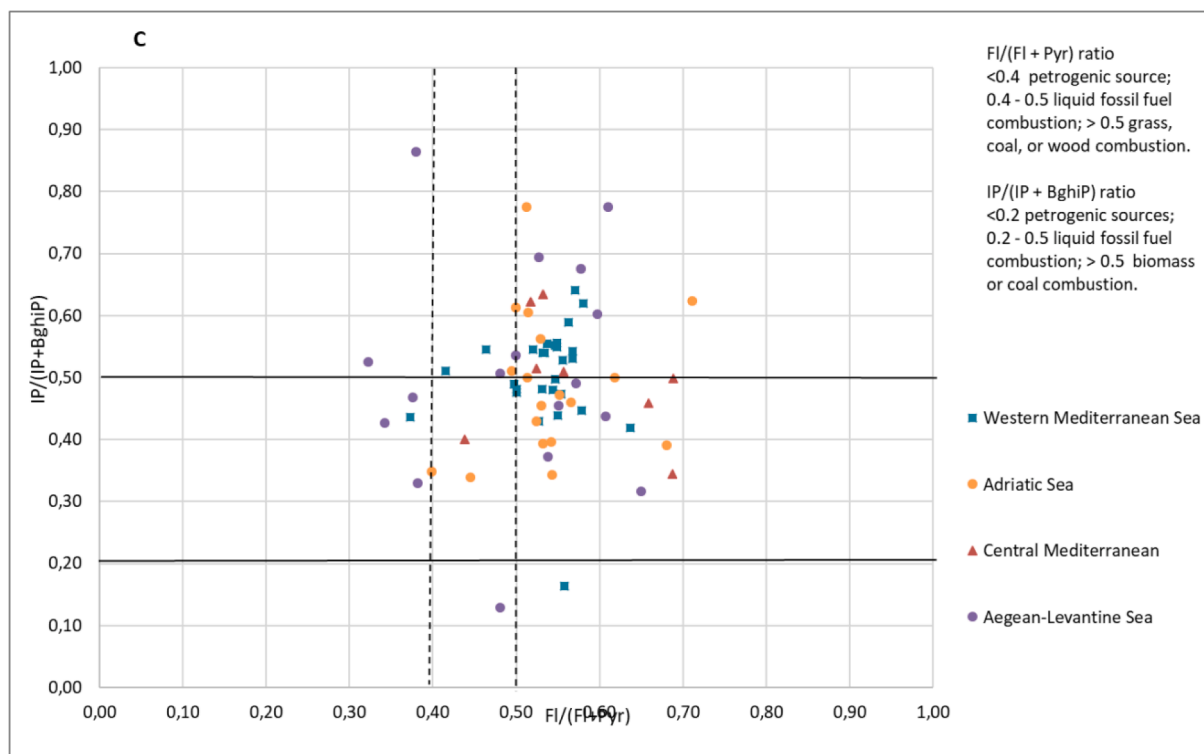


Fig. 4. (continued).

based index series (see Table 3). Remind that we considered a first-time difference of the log-concentration values, thus the temporal series length  $T$  is equal to 29 years. We tested the null  $H_0 : \rho_0 = \dots = \rho_8 = 0$ , consequently the Ljung-Box Q-statistic follows a chi-square distribution with 9 degrees of freedom under the null.

Note that if we apply the conservative Holm–Bonferroni’s correction to adjust the p-values for multiple testing comparison (Bretz et al., 2011), we get likewise strong evidence against independence for all compounds, with the only exception of naphthalene, for which the greater adjusted p-value is 0.037. This could be related to difficulties associated with the analytical procedures (i.e., low recoveries, high background levels) that lead to a less precise quantification of naphthalene in environmental samples (Yamada et al., 2009; Gao et al., 2013; Wang et al., 2014). To sum up, these test results confirm the rightness of our conjecture on PAH concentrations.

Climate change poses a considerable threat to the Mediterranean area, exacerbating existing environmental problems (Turco et al., 2018). Seasonal changes in precipitation rates and temperature will have an impact on coastal and marine ecosystems as well as on forests. More frequent fire events resulting from increasing heat waves will further reduce water quality and will affect marine communities. Warming, droughts, and extreme events in coastal areas put additional pressure on marine ecosystems that are already heavily impacted by industrial pollution and urban growth. Thus, coastal pollution continues to represent a critical threat to many parts of the Mediterranean region. Historical documentation of anthropogenic impacts near the Mediterranean coasts has been undertaken by Tamburrino et al. (2019) and Combi et al. (2020). Despite efforts towards a cleaner Mediterranean, EEA Report 7/2020 makes clear that the region still needs to take serious action to avoid jeopardising current progress towards reducing the main sources of pollution. Our reliance on a well-functioning marine and coastal environment should make it clear that it is becoming more urgent to implement ecosystem-based management to reduce environmental pressure and protect fragile Mediterranean ecosystems.

### 3.4. Origin of PAH contamination

The use of PAHs diagnostic ratios is the most common approach for the identification of the origin of the contamination, thanks to its simplicity. These ratios are applicable to PAH measured in samples from different environmental matrices, albeit with limitations, as pointed out by Tobiszewski and Namieśnik (2012). This methodology is based on the assumption that different sources emit PAHs at the same ratio, and that such ratio remains constant since PAHs, with the same molecular weight, have a similar environmental fate and behavior (Katsoyiannis and Breivik, 2014). Various authors raised several concerns about the ability of these ratios to properly assess the PAHs origin, since PAHs concentrations values may vary from their sources to the receptors as a function of reactions in the environment (Zhang et al., 2005; Katsoyiannis et al., 2011). In particular, Ant/(Ant + Phe) ratio is the most susceptible to atmospheric processes, together with BaA/(BaA + Chr), that are reported to be remarkably sensitive to environmental changes. On the other hand, FL/(FL + Pyr) and IP/(IP + BghiP) are more conservative ratios. Since most environmental samples contain PAHs from mixed sources, the application of a single ratio can lead to misleading results (Yunker et al., 2002). Considering the high number of PAHs analysed, the inspection of additional ratios gives a more reliable and accurate interpretation. Despite the recognised uncertainties and criticality of this approach, in this paper PAH ratios were plotted against each other to provide information on sources (Fig. 4). The Fig. 4 shows the FL/(FL + Pyr) ratio for all observations present in the dataset. Most of the samples from the Western Mediterranean, Adriatic Sea, and Central Mediterranean (77%, 75%, and 64%, respectively) showed a ratio  $> 0.5$ , whereas the ratio showed a scattered distribution of values for samples from the Aegean–Levantine basin, with a value  $> 0.5$  in only 55% of the observations. As reported by Yunker et al. (2002), a FL/(FL + Pyr) value  $< 0.4$  indicates a petrogenic source, whereas a value between 0.4 and 0.5 suggests liquid fossil fuel combustion, and a ratio over 0.5 generally indicates grass, coal, or wood. Only few observations found a FL/(FL +

Pyr) ratio < 0.4 (8%, 5%, 29%, and 20% for the Western Mediterranean, Adriatic, Central Mediterranean, and Aegean–Levantine basins, respectively); such a ratio is a good indicator of crude oil contamination (Hartwell et al., 2020). Introduction of petroleum products into the marine environment may occur due to the discharge of industrial effluents, the activity of oil refineries, or accidental oil spills, and is a cause of great concern. In the present study, Fl/(Fl + Pyr) ratios < 0.4 were always found in areas around petroleum refineries or characterised by production, storage, and transportation of gas/oil. Such areas included the Sfax–Kerkennah coastal zone in Tunisia (Central Mediterranean), the Adriatic Sea, the Central Mediterranean portion of the Egyptian coast, and the Mediterranean coast of Israel (Aegean–Levantine basin).

The Ant/(Ant + Phen) ratio (y-axis in Fig. 3A), showed a value > 0.1 in most of the samples (85% in the Western Mediterranean, 85% for the Adriatic Sea, 86% for the Central Mediterranean, and 80% for the Aegean–Levantine basin). This was consistent with a pyrogenic origin.

With regard to the BaA/(BaA + Chr) ratio (y-axis in Fig. 3B), the majority of data collected (92%, 90%, 67%, and 76% in the Western Mediterranean, Adriatic Sea, Central Mediterranean Sea, and Aegean–Levantine Sea, respectively) showed a ratio above 0.35. According to Hartwell et al. (2020), a BaA/(BaA + Chr) ratio > 0.35 is characteristic of combustion sources, whereas a ratio lower than 0.2 indicates petroleum sources, and a ratio between 0.2 and 0.35 may imply either petrogenic origin or combustion. In our study, samples showing a BaA/(BaA + Chr) value < 0.2 came primarily from industrial areas, harbours, or zones affected by petroleum contamination; such contamination could be due to storage of crude oil, boating activities, or intense marine traffic. Such areas included the Sfax–Kerkennah channel in Tunisia (southern Central Mediterranean basin), the industrial harbour of Augusta in Sicily (Western Mediterranean basin), and the Turkish coast (Aegean–Levantine basin).

The IP/(IP + BghiP) ratio was > 0.5, indicating mixed sources, in 55% of observations from the Western Mediterranean, 33% of samples from the Adriatic Sea, 50% of samples from the Central Mediterranean, and 50% of observations from the Aegean–Levantine basin (y-axis in Fig. 3C). This ratio showed values between 0.2 and 0.5 in 41%, 67%, 50%, and 44% of observations from the Western Mediterranean, Adriatic, Central Mediterranean, and Aegean–Levantine basins, respectively. An IP/(IP + BghiP) ratio < 0.2 is characteristic of petrogenic sources, whereas a ratio between 0.2 and 0.5 indicates liquid fossil fuel combustion, and a value higher than 0.5 indicates combustion of biomass or coal (Syakti et al., 2015).

Although the data analysed in this study came from different projects and different authors, were subjected to different analytical techniques, and were collected over a long period of time, the indices applied to this dataset uniformly indicate a pyrogenic origin for most PAHs in the Mediterranean. Moreover, our analysis supports the hypothesis that there is negligible variability in emission sources among the four basins of the Mediterranean. The PAH diagnostic ratios point towards burning of plant material, suggesting that most PAHs in Mediterranean sediments are formed as a consequence of forest and prairie fires. Indeed, Giannaros et al. (2021) provided evidence that the Mediterranean climate is becoming warmer and drier, facilitating extreme fire weather conditions. Although the majority of wildfires are a consequence of human activity, the impact of fires in Mediterranean Europe varies from year to year, mainly because of weather conditions (Camia et al., 2017). Given the relationship between forest fires and PAH release, these changes in wildfire regimes may cause further deterioration in marine ecosystem quality.

In light of these considerations, it is clear that biomass burning contributes significantly to the emission of PAHs in the Mediterranean, especially in the Western Mediterranean basin (which includes the Iberian Peninsula and Sicily). Thanks to winds that blow from the Iberian Peninsula toward the rest of the Western Mediterranean (Accadia et al., 2007), PAHs produced during these fire events can be transported from forests and prairies via the atmosphere, reach the marine system,

and accumulate in sediments. Aside from wind, precipitation after a fire is also very effective in transporting sorbed PAHs. According to a study conducted in Catalonia (Vila-Escalé et al., 2007), the concentrations of PAHs in a creek increased after a fire event, showing peaks after precipitation due to subsequent runoff, leaching, and soil erosion. PAH concentrations did not return to background levels until one year after the event. Thus, water runoff from soils in burned areas can contribute to PAH loads for a long period of time.

Analysis of PAH ratios showed that aside from biomass burning, combustion of coal and liquid fossil fuels also contributed to release of PAHs into the Mediterranean. Fossil fuel burning is the dominant source of PAH emissions in sites near urban centres or harbours. In the Western Mediterranean, such sites include the Gulf of Lion and the Bay of Marseille (France), Olbia harbour (Italy), and the Gulf of Milazzo (southern Italy); in the northern Adriatic, the Venice Lagoon and the Gulf of Trieste; in the Central Mediterranean, the Sfax–Kerkennah channel in Tunisia; and in the Aegean–Levantine region, the Egyptian coast west of Alexandria and the Aegean coast of Turkey. Road traffic coupled with intense marine traffic and nautical tourism is often typical of this type of site. The role of ship traffic and harbour activities on particulate PAH emissions is well known, and it has been documented, for example, in the Venice Lagoon (Gregoris et al., 2015) and the Gulf of Trieste (Bajt, 2014). Ships release a large quantity of PAHs into the surrounding area, especially during harbour approaches and stops (Cooper, 2001). The problem does not concern only sites known as centres of maritime tourism; a study conducted on Ustica, an island located in the southwestern Tyrrhenian Sea and characterised by the absence of industrial activity or river discharge, demonstrated the influence of ferryboat traffic, particularly in the most proximate site to the port of Ustica (Berto et al., 2009).

### 3.5. Ecological risk

Using SQGs, we performed screening-level risk assessments in order to determine whether PAH concentrations pose an acceptable, concerning, or unacceptable risk to the benthic marine community in each basin of the Mediterranean Sea. Comparing the measured concentrations with the ERM showed that for all PAHs investigated, the Western Mediterranean basin had the highest percentage of observations that indicated concentrations with a high or very high potential to induce adverse effects in the benthic marine community, with all 12 compounds displaying percentage values falling into the unacceptable risk band. In the Central Mediterranean, 8 of the 12 PAHs showed concentrations falling into the unacceptable risk band. In the Aegean–Levantine zone, only 4 PAHs posed a high risk to the benthic community, whereas only two PAHs presented an unacceptable risk in the Adriatic Sea. More specifically, the percentage of observations in which measured concentration exceeded ERM ranged from 3% to 8% for individual PAHs in the Western Mediterranean, from 0% to 13% in the Central Mediterranean, from 0% to 5% in the Aegean–Levantine basin, and from 0% to 2% in the Adriatic Sea.

Ecological risk assessment based on the PEL threshold revealed that concentrations exceeded PEL for all 12 PAHs in the Western Mediterranean, for 11 PAHs in the Adriatic Sea and Central Mediterranean (the only exception was Nap), and for 10 compounds in the Aegean–Levantine basin. The percentage of observations in which measured concentration exceeded PEL ranged from 5% to 6% for individual PAHs in the Western Mediterranean, from 0% to 17% in the Central Mediterranean, from 0% to 13% in the Aegean–Levantine basin, and from 0% to 4% in the Adriatic Sea.

The greatest concern raised by these results stems from the fact that not all observations indicating high risk were derived from zones subjected to high anthropogenic pressure, such as megacities, harbours, and industrial areas. On the contrary, areas treated as control sites also fell into the high-risk band (this is the case, for example, for BghiP in the Aegean–Levantine basin). This result suggests a link between the main

source of PAH contamination (biomass burning) and PAH concentrations posing an unacceptable risk, as the basins where such critical situations occur most often were also characterised by the highest impact of PAHs. The Western Mediterranean basin in particular has been subject to the highest rate of environmental alteration, mainly due to the growth of tourism. High levels of urbanisation and industrialisation in this region have led to the development of maritime industries, shipping, and energy, which have put pressure on resources, resulting in degradation of the aquatic ecosystem and localised pollution. All these changes have resulted in greater emissions of pollutants, including PAHs, at concentrations that could pose a risk for the marine community.

Fig. S5 shows the results of the application of the hazard ranking scheme described in Section 2.3 to this dataset. The Western Mediterranean basin was in the worst condition, with concentrations of each individual PAH posing a severe hazard to benthic marine communities, as up to 10% of concentration values (in red in the figure) are above the high hazard threshold. Moving eastward, the number of single compounds posing an ecologically unacceptable risk decreased. There were differences in hazard classification depending on whether ERM or PEL was used, with the latter one producing more severe classifications. In the Central Mediterranean, most PAHs showed quotients indicating that they posed a risk to the benthic community, with the exception of Nap alone (when PEL was used) or the four lighter PAHs (when ERM was used). However, for the Aegean–Levantine basin and the Adriatic Sea, the results indicated a low hazard for almost all compounds, regardless of the approach used.

A few objections to the use of ERM and ERL to calculate the sediment quality index have been expressed. Some researchers and managers preferably suggest the use of the combination of sediment chemistry, sediment toxicity, and benthic community's conditions to assess sediment quality (US EPA, 2012). An alternative view for the sediment quality index stated that the determination of a poor level of sediment condition should be based on the joint occurrence of elevated sediment contaminant concentrations and high sediment toxicity. O'Connor et al. (1998), O'Connor et al. (2000) and Ingersoll and Wenning (2002),

indeed, reported that the ERM or ERL exceedance does not always coincide with toxicity. Despite these criticisms, these authors themselves confirmed the correlation between an increase in the incidence of toxicity with an increasing number of ERM exceeded. It should be reminded that ERM and PEL are an assessment of the concentration of a chemical that could determine adverse biological effects at 50th and 10th percentile, respectively. These values are routinely used as guidelines for the prediction of a potential adverse effect due to sediment contamination and they are useful tools for risk assessment managers to identify areas and/or samples that require further investigation.

The application of empirical SQGs, such as those utilised in this study, allows the prediction of thresholds at which toxicity to benthic organisms is probable, giving a first insight into the hazard posed by contaminants. However, such SQGs do not provide a perspective on the risk and possible negative outcomes associated with toxin concentration levels. To integrate the results obtained using SQGs and analyse trends of risk, we also calculated the RQ for the eight PAHs for which EQS guidelines are available (Fig. 5). The results indicate that risk differs between the Western Mediterranean and the other three basins. RQ values for all PAHs in the Adriatic, Central Mediterranean, and Aegean–Levantine basins indicated low risk from 2007 to 2017. Moreover, RQ values for the Adriatic Sea were generally below the risk level throughout the entire period, with a few exceptions: an  $RQ > 1$  was found for all PAHs in two years (1992 and 1997), for BaP in 2012, for BbF and Fl from 2003 to 2006, and for BkF in 2003, 2006, and 2012. In the Aegean–Levantine basin,  $RQ < 1$  for almost all PAHs; the only exceptions were Ant and BaP, which exceeded the thresholds in most years. Similarly, in the Central Mediterranean, an  $RQ > 1$  was found for the majority of PAHs until the first years of the 2000 s, which was followed by a continuous decrease in concentrations until 2013. Although the Central Mediterranean was the basin with the second highest PAH concentration, RQs up to 2–3 orders of magnitude lower than EQS thresholds were measured in more recent years. An opposite situation seems to characterise the Western Mediterranean basin, where the situation is most concerning. The RQs of the eight PAHs straddled the risk threshold from 1985 to the first year of 2000 and, after a sudden

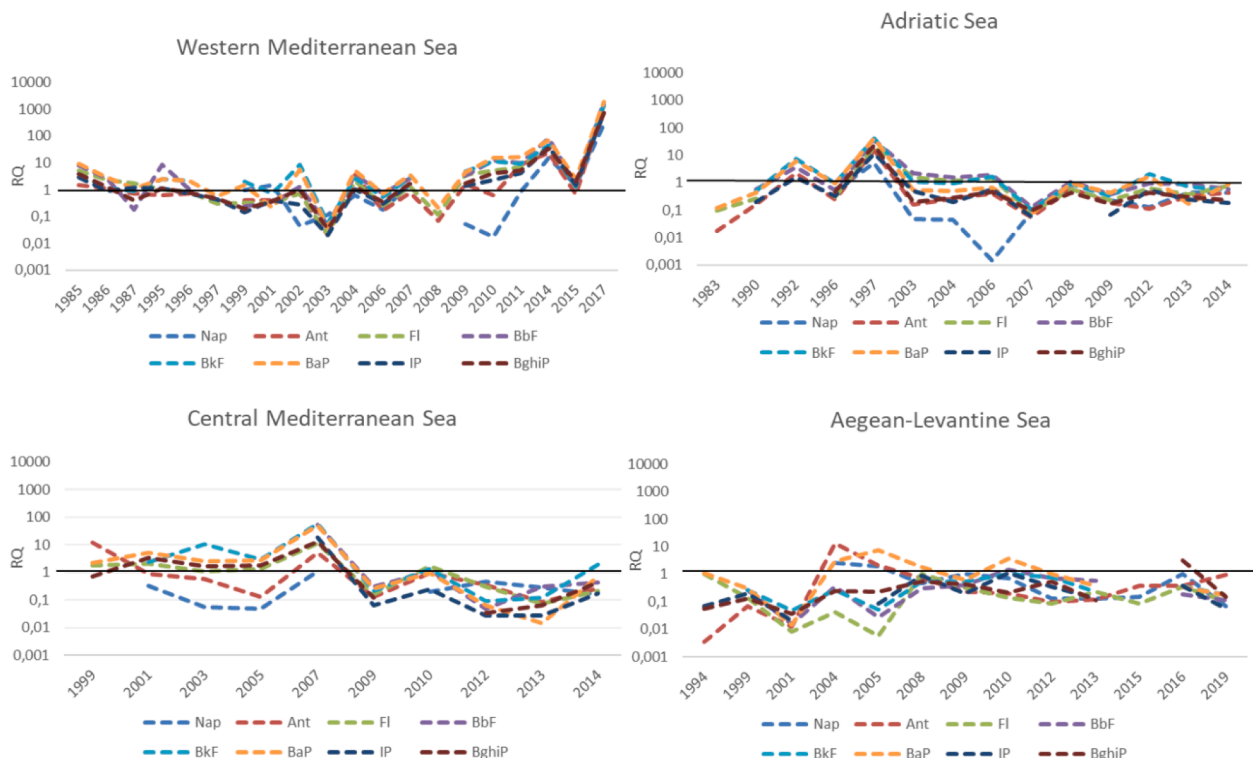


Fig. 5. Temporal trend of risk quotient for the eight PAHs regulated by Directive 2013/39/EU.

decrease in 2003, continued to increase. The increasing trend in RQs indicates that the quality of this area is of very high concern, as the RQs exceeded the risk threshold by two or three orders of magnitude. Indeed, as discussed in Section 3.3, the temporal trends of PAH concentrations in this area of the Mediterranean Sea show a statistically significant increase in recent years (see Table 2).

#### 4. Conclusions

During the last decades of the 20th century, the increased pressure of human activities resulted in environmental degradation of the Mediterranean Sea region, resulting in drastic alterations of the structure and functioning of this precious ecosystem. This problem has been exacerbated by the accumulation of contaminants in sediments, which act as both a sink and source of pollutants even long after the source of pollution has been abated. In our study, starting from a review of literature data, we reconstructed the spatial distribution of concentrations and sources for 16 priority PAHs in sediments of the four basins of the Mediterranean Sea. The temporal trend of risk to the benthic marine community was also assessed. Spatial and temporal analysis revealed that PAH concentrations in sediments of the Mediterranean Sea are still very high, particularly in the Western Mediterranean, where the temporal trend of risk to the benthic marine community is increasing. We advocate the use of additive models for the estimation of non-linear trends owing to their great flexibility in determining the shape of the trend and its confidence bands. Finally, our analysis suggests that the primary source of PAHs in the Mediterranean Sea is biomass burning, with a further contribution from combustion of coal and liquid fossil fuels. These results suggest the need for stronger efforts to reduce the release of pollutants into the Mediterranean Sea.

Megacities and ports deserve particular attention as they are points of concern; measures to reduce the release of pollutants from industrial sectors or the improper disposal of hazardous waste and to reduce the shipping and port activities' emission improving port management practices should be implemented. Moreover, wildfires prevention should be a priority in landscape planning in all countries bordering the Mediterranean considering the assessed significant positive correlation between annual growth rates of PAH concentration in sediment and wildfires. It can be suggested to adopt both short- and long-term fire prevention measures such as the reintroduction of grazing animals (both wild and domesticated animals are very effective and efficient in reducing fuel by consuming different plant material for food), the conversion of artificial and simplified ecosystems into more natural and diversified forests. The increase of public awareness on forest fire risk should be improved, to prevent unwanted human-caused fires.

#### CRedit authorship contribution statement

**C. Rizzi:** Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing - original draft. **S. Villa:** Conceptualization, Project administration, Supervision, Writing - review & editing. **C. Chimera:** Data curation. **A. Finizio:** Conceptualization, Supervision, Writing - review & editing. **G.S. Monti:** Formal analysis, Data curation, Software, Writing - review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ecolind.2021.107923>.

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